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16 Aug 17

MEMORANDUM FOR U.S. EPA Region IX
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Arizona Department of Environmental Quality (ADEQ)
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FROM: AFCEC/ CIBW
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SUBJECT: Submission of "Review of Praxis Environmental Technologies, Inc. memorandum dated 22 May 2017, Time of Remediation Estimates, Enhanced Bioremediation at ST012, Former Williams Air Force Base, Mesa, Arizona"

1. The Air Force is pleased to submit the attached document: *Review of Praxis Environmental Technologies, Inc. memorandum dated 22 May 2017, Time of Remediation Estimates, Enhanced Bioremediation at ST012, Former Williams Air Force Base, Mesa, Arizona.* The technical memorandum was issued with an ADEQ and EPA cover letter dated 30 May 2017.

2. The Air Force review of the Time of Remediation Estimates memorandum provides discussion and rationale for agreements and disagreements with the applied concepts and assumptions as well as the utility of the model. The Air Force review document is being issued under separate cover from the Revised Draft Final Addendum #2, Remedial Design and Remedial Action Work Plan for Operable Unit 2, Revised Groundwater Remedy, Site ST012. Please contact me at (315) 356-0810 or by email at catherine.jerrard@us.af.mil if you have any questions regarding the Air Force review document.

CATHERINE JERRARD, PE
BRAC Environmental Coordinator

Attachment:

Review of Praxis Environmental Technologies, Inc. memorandum dated 22 May 2017, Time of Remediation Estimates, Enhanced Bioremediation at ST012, Former Williams Air Force Base, Mesa, Arizona

c: ADEQ – Wayne Miller (2 and 2 CD)
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REVIEW OF PRAXIS ENVIRONMENTAL TECHNOLOGIES, INC., DATED 22 MAY 2017
"TIME OF REMEDIATION ESTIMATES, ENHANCED BIOREMEDIATION AT ST012"
SITE ST012
FORMER WILLIAMS AIR FORCE BASE
MESA, ARIZONA

Purpose

The purpose of this document is to convey our review of the memorandum (memo) titled "Time of Remediation Estimates, Enhanced Bioremediation at ST012", prepared by Dr. Lloyd "Bo" Stewart of Praxis Environmental Technologies, Inc. located in Burlingame, California. The review presented herein is not intended to provide general or specific comments for revision of the document; but, is instead intended to provide discussion and rationale for agreements and disagreements with the concepts and assumptions that were applied, as well as the utility of the model to estimate time of remediation (TOR).

Background

Over the decades of Remedial Investigation/Feasibility Study work conducted at ST012, evidence of depleted groundwater sulfate concentrations relative to ambient levels have been observed in the hydrostratigraphic zones impacted with non-aqueous phase liquid (NAPL). The differences in sulfate concentrations between background and NAPL-impacted zones range between approximately 200 and 300 milligrams per liter (mg/L). Given the flux of naturally occuring soluble terminal electron acceptors (TEA) into ST012, this utilization of sulfate represents the largest fraction of petroleum-hydrocarbon biodegradation by the available TEAs. It has been estimated that sulfate reduction accounts for more than 80 percent of the naturally occuring petroleum hydrocarbon biodegradation at ST012 (BEM, 1998). Alhough naturally-occuring sulfate reduction of the petroleum hydrocarbon contamination is significant, it is also limited by the natural flux of sulfate supplied by upgradient groundwater.

Technical Evaluation of TOR Estimates

The conclusions made in the joint U.S. Environmental Protection Agency (EPA)/Arizona Department of Environmental Quality (ADEQ) cover letter to the TOR memo do not appear to be direct conclusions from the TOR memo. Specifically, the TOR memo evaluates various scenarios in the sensitivity analysis, but does not conclude which scenario is most representative. Rather, the TOR memo concludes with a series of questions in **Section 6** that should be evaluated in initial Enhanced Bioremediation (EBR) phases. In contrast, the joint EPA/ADEQ cover letter concludes that, "realistic remedial timeframes for enhanced bioremediation to degrade contaminants remaining at the ST-12 Fuel Spill site range from 100 to 200 years for the Upper Water Bearing Zone and 30 to 50 years for the Lower Saturated Zone."

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The Air Force finds that the long TOR estimates (many decades to centuries) are based on many conservative inputs that are likely not representative of EBR. Alternate representative inputs are supportive of the timeframes presented in the Remedial Design and Remedial Action Work Plan (RD/RAWP). Specific instances of conservative inputs to the TOR estimates are as follows:

- Porosity values of 0.4 are overly conservative. In the Thermal Enhanced Extraction (TEE) Report source assessment calculations, maximum values for total porosity in individual silt/clay layers were 0.35. TEE modeling used a porosity of 0.3. (BEM, 2011).
- Endpoint modeling concentration of groundwater in direct contact with light non- aqueous phase liquid (LNAPL) (acknowledged as the most stringent interpretation in the TOR memo).
- Biodegradation of the solid- and liquid-phase hydrocarbons is zero. Only dissolved-phase petroleum hydrocarbon contamination is bioavailable.
- Rate-limited or non-equilibrium NAPL mass transfer from the liquid-to dissolved-phase under EBR does not consider biological-enhancement of NAPL dissolution.
- First-order and Monod sulfate-biodegradation rate constants are overly conservative as they represent the low end of natural (unenhanced) conditions. These should not be used in the context of EBR expectations.
- The scaling approach provided in **Appendix C** of the memo, and used to arrive at a benzene mass transfer coefficient of 0.0042 day^{-1} is overly conservative as a mass transfer coefficient representative of natural or ambient biodegradation. The scaling approach considers a correlation between the mass transfer coefficient and the Sherwood Number, which is one of approximately 10 dimensional variables used to define inter-phase mass transfer rate from a LNAPL to mobile aqueous phase. The version of the Sherwood-Number/mass-transfer coefficient correlation applied to the scaling approach was arrived at through analysis of data from column studies conducted at flow rates between about 3 and 15 meters per day (m/d). While the interstitial velocities generated during the on-site mass transfer test (MTT) (Mobile et al, 2016) approach the column-study velocities, the ambient velocity is far below those during the MTT or the column studies and the correlation is likely not applicable for scaling.
- The one-time, 8,000 mg/L application of sulfate does not acknowledge the proposed phased EBR approach which may consist of multiple rounds of injection if needed. The application of conservative assumptions with respect to mass presence combined with limiting sulfate application prolongs the TOR.

Of these inputs, the last three (low biodegradation rate kinetics, low mass transfer coefficient, and one-time 8,000 mg/L sulfate application) dominate in their effect on generating longer TOR estimates. Further discussion of several of these major points are presented in the follow paragraphs.

The TOR memo presents a screening-level evaluation for TOR estimates; as such, it includes simplified assumptions and generalizations. **Section 1** of the memo presents a conceptual site model (CSM) that describes the generalized geometry and hydrogeology of the subsurface at ST012. The CSM narrative and assumptions for use in the screening-level evaluation are appropriate although newer information on water table rise is available. Similarly, the assumptions and estimates for the NAPL volume and composition and the calculation of endpoint for modeling remediation presented in **Sections 2 and 3** of the memo are appropriate for a screening-level evaluation, with the caveats noted above concerning the conservative nature of the 0.4 porosity and the endpoint calculation method.

Section 4 of the TOR memo presents assumptions and calculations used to estimate TOR utilizing the local equilibrium (LE) model approach. The memo conveys that if LNAPL and groundwater maintain equilibrium and benzene biodegradation rates can be sustained at 0.0125 day^{-1}, then the remedial goal (RG) for benzene would be achieved in about 12 and 16 years in the LSZ and UWBZ, respectively. The screening-level approach used to estimate TOR does not consider soil-water and NAPL-soil partitioning of petroleum-hydrocarbons; solid- and NAPL-phase biodegradation; biological growth; and, Monod kinetics of sulfate and petroleum hydrocarbon utilization. These factors/models that are not considered likely represent a smaller, less significant impact to the overall TOR estimate than the LNAPL-groundwater equilibrium fraction considered. Near equilibrium conditions are likely under ambient conditions in aquifer material impacted with LNAPL; except possibly in areas where NAPL saturations have been reduced by Steam Enhanced Extraction, and where the ambient flux of TEAs that are more thermodynamically favorable than sulfate (e.g., oxygen) could exceed the TEA utilization.

Aquifer Zone	Calculated Target NAPL Volume Porosity=0.3 years	Calculated Target NAPL Volume Porosity=0.4 years	Literature Target NAPL Volume Porosity=0.3 years	Literature Target NAPL Volume Porosity=0.4 years
$\lambda = 0.0125\ d^{-1}$				
UWBZ	16.1	10.4	19.0	19.5
LSZ	11.8	7.8	24.3	26.7
$\lambda = 0.03\ d^{-1}$				
UWBZ	7.0	4.5	8.2	8.4
LSZ	5.4	3.5	11.1	12.0
$\lambda = 0.00038\ d^{-1}$				
UWBZ	170	132	200	245
LSZ	67	55	136	182

Figure 1 LE Model Sensitivity Analysis Results with Remedial Action Outcome (Green=overachieving, yellow=expected range, red=underachieving)

Section 4 also includes sensitivity analysis of TOR estimates considering the first-order biodegradation rate and the total porosity. As expected, longer TOR is estimated for higher total porosity values and lower biodegradation rates; and, shorter TOR is estimated for lower porosities and higher biodegradation rates. The TOR estimates considering the parameter sensitivity range for benzene biodegradation rate and porosity values represent unlikely conditions that either overachieve or underachieve the remedial action objective. Figure 1 was developed using **Table 6** from the memo.

It is likely that implementing EBR will biologically enhance the dissolution of LNAPL (Chu et al, 2006). The increase in biologically enhanced LNAPL dissolution by EBR will maintain LNAPL mass transfer at rates that approach those estimated by the LE model until groundwater chemicals of concern (COCs) reach RGs. This is conceptualized by the screening-level estimates described in **Section 4** of the memo. Therefore, the LE model presented in **Section 4** of the memo provides an appropriate screening-level evaluation of the EBR design approach. Other researchers have implemented the LE model to assess biologically enhanced LNAPL dissolution in porous media (Bahar et al, 2016).

EBR, primarily by the addition of TEA, is designed to achieve/maintain equilibrium as described by the LE model. The ST012 EBR design relies on advective and dispersive transport in the active phase and diffusive transport in the immobile, inactive phases; as well as enhanced sulfate respiration that maintains NAPL-water-soil equilibrium until groundwater COCs have achieved RGs. Researchers have measured biological enhancement of LNAPL dissolution that result in up to a 16 time increase of the abiotic mass transfer coefficient (Amos, 2008; Cope, 2001).

Section 5 presents the non-equilibrium (NE) LNAPL dissolution approach screening-level models and the NE rationale, assumptions, TOR estimates, and sensitivity analysis. The NE model is used to estimate TOR considering EBR that does not enhance NAPL dissolution, and the rate of LNAPL dissolution is restrained below equilibrium due to abiotic, site-specific limiting factors. The NE TOR estimates are also compared to the LE TOR estimates in **Table 7** of the memo. At the LNAPL dissolution rates determined in the on-site testing (Mobile et al, 2016), the NE model TOR estimates are approximately equal to the LE model TOR estimates. Considering:

1. the lumped mass transfer rates for benzene determined at the site (Mobile et al, 2016);
2. a sustainable first-order biodegradation rate for benzene; and
3. the screening-level assessment presented in the model (summarized in **Table 7**).

LNAPL dissolution and biodegradation rates that are limited only by LNAPL dissolution equilibrium are readily achievable. The increase in LNAPL dissolution anticipated by EBR will likely maintain LNAPL dissolution rates at equilibrium conditions throughout the TOR.

Besides rate-limited LNAPL dissolution, the major differences between the LE and NE screening models that use first-order biodegradation are:

1. Retardation or partitioning of petroleum hydrocarbon mass between soil and water was included in the NE model; however, the retardation and/or the distribution coefficient was not reported in the memo.
2. The NE model considered multiple soluble components (31 components of the LNAPL) whereas the LE model was simplified with only two NAPL components; benzene and the remainder of the LNAPL as an insoluble liquid. The description of the approach is provided in **Appendix B** of the memo.

The NE model relies on a LNAPL mass transfer term to estimate LNAPL dissolution rates. The mass transfer term is considered to be independent of biodegradation; it is considered an abiotic reactive-transport term. The mass transfer term in the screening model includes a lumped coefficient that accounts for the combined effects of hydrodynamics, dispersion, interfacial area, and diffusion on mass transfer over the volume of the LNAPL-impacted aquifer being modeled. Research conducted on NE LNAPL dissolution report two types of mass transfer coefficients for non-reactive LNAPL dissolution; the major difference between them is the inclusion of the interfacial area between phases. The mass transfer coefficient used in the screening model includes the interfacial area per unit volume of porous media impacted by LNAPL and it is expressed in units of per time.

The lumped mass transfer coefficients used in the multi-component screening models presented in **Section 5** of the memo were estimated by analysis of testing conducted at the site and were scaled as described in **Appendix C** of the memo. The methods used to scale the mass transfer coefficient estimates from on-site testing consider the differences between current/ambient site conditions and the conditions at the time of the test. The scaling of the mass transfer coefficient to current site conditions considered the difference in LNAPL saturation and the pore volume exchange rate. The mass transfer coefficient scaling approach was customized from research (Clement et al, 2004; Powers et al, 1994) and attempted to take into account the difference in LNAPL saturation and the pore volume exchange rate as a substitute for interstitial water velocity between the on-site test and the current/ambient conditions.

The approach to scaling of the mass transfer coefficient values from the test to current conditions considering LNAPL saturation is reasonable and acknowledges that mass transfer rates are transient and proportional to LNAPL saturation (Powers et al, 1994). Moreover, it is acknowledged that without biological enhancement of LNAPL dissolution, the mass transfer rates of NAPL components will likely decrease with the ambient depletion of LNAPL saturations.

A major assumption in **Appendix C** sets the baseline of the mass transfer coefficient determined by the on-site test at 0.05 day^{-1}. This baseline value for the mass transfer coefficient is highly conservative; the mass transfer coefficients determined as a result of the on-site test were 0.6, 0.4, and 0.022 day^{-1}. Referring to the method applied to scale mass transfer coefficients (Clement et al, 2004), the maximum value of 0.6 day^{-1}, not a minimum value, is likely more appropriate for scaling.

The scaling of the mass transfer coefficient values from the test to current conditions considering the pore volume exchange rate is exceedingly conservative and may not have been correctly applied. The MTT paper (Mobile et al, 2016) stated that, "…pore velocity should have negligible impact on predicted values of $K_l^{N.}$". Nevertheless, the TOR memo presents an approach to interstitial-pore-water-velocity scaling of the mass transfer coefficient in **Appendix C,** which is based on the modified Sherwood Number correlation developed using experimental data from column studies (Powers et al, 1994). The modified Sherwood Number correlation includes the Reynolds Number, which is a function of the interstitial aqueous velocity, among other variables. Although the use of the pore volume exchange rate is an acceptable substitute for interstitial pore water velocity for the screening model, the application of the correlation for scaling based on pore water velocity is likely not. The scaling of the lumped mass transfer coefficient to variation in pore volume exchange rate in **Appendix C** may not consider the experimental design and analysis conducted to arrive at the modified Sherwood Number correlation (Powers et al, 1994) and the differences compared to the MTT or full-scale EBR.

The modified Sherwood Number correlation developed for steady-state NAPL dissolution rates (Powers et al, 1991) was used as the foundation for transient LNAPL dissolution (Powers et al, 1994). In development of the modified Sherwood Number correlation for transient LNAPL dissolution, the experiments were run at aqueous flow velocities between approximately 3 and 15 m/d. Analyses of the experimental data were conducted to assess the impact of grain size, grain size distribution, and LNAPL saturation on LNAPL dissolution rate. To analyze the impact of these variables on LNAPL dissolution, the data were grouped by tests of similar interstitial aqueous velocities, thereby discounting the impact of the velocities on the comparisons. As such, it is likely that using the modified Sherwood Number correlation developed by Powers in 1994 is not suitable for scaling the mass transfer coefficient to different pore water velocities.

Research on the effects of pore water velocity on LNAPL dissolution has been published (Seagren, 2003). The results of the research show that the LE model predicts that the LNAPL dissolution will increase indefinitely as groundwater flow velocity increases. Accordingly, based on the LE model, it would be reasonable to assume that the more the groundwater velocity is increased, the greater the dissolution flux and mass rate of NAPL removal will be. However, the NE model predictions demarcate a point of diminishing returns. As groundwater velocity increases, a reduced rate of enhancement of LNAPL dissolution occurs and there is little gain in increasing the average pore water velocity above this point. The research concluded that the LE and NE model predictions for LNAPL dissolution converge at average pore water velocities below approximately 10 m/d. The average pore water velocities at ambient conditions and those induced during the on-site MTT test are significantly less than 10 m/d at approximately 0.02 and 0.9 m/d, respectively.

Previous research has evaluated when the LE and NE model predictions converge (Seagren et al, 1999). In this research, the convergence of the LE and NE models is dependent on the value of the product of the modified Sherwood Number and the Stanton Number, another dimensional variable used in the theoretical rationalization of the mass transfer term. This research concluded that the equilibrium boundary condition was invalid for high velocities (20 m/d), which are approximately 100 times greater than the ambient velocities at the site (0.02 m/d). The research also concluded that for conditions that yield a large product of the modified Sherwood and Stanton Numbers, which can be brought about by small interstitial pore velocity, the NE and LE models converge. The conditions under which the LE assumption is appropriate include significant contact between the flowing groundwater and the NAPL contamination, low pore water velocity and residual NAPL saturations. These conditions for appropriate application of LE are similar to conditions at the site, especially when comparing to the experimental study conditions used by researchers to develop dimensional-variable correlations used to define the mass transfer term.

Section 5 of the memo includes additional TOR estimates that include/consider microbial growth kinetics and Monod kinetics to model the utilization of sulfate and hydrocarbon species of the LNAPL. In this part of **Section 5** abbreviated sensitivity analysis was conducted considering a range of values for porosity and LNAPL volume similar to the sensitivity analysis conducted for the LE model; however, TOR estimate sensitivity to the high-end mass transfer coefficient from the MTT was not presented. Sensitivity to variability in Monod kinetics was conducted in this section of the memo; however, it is unclear if the half-saturation concentrations and the maximum utilization rates were varied or just the maximum utilization rates. Additional sensitivity analysis to the mass transfer and Monod kinetics coefficients would be useful for the completeness of the screening level assessment. Currently, the last part of **Section 5**, which considers Monod and microbial growth kinetics only evaluates the low end of the mass transfer coefficient values assessed in the other portions of the memo.

Conclusion

Overall, the following general conclusions can be made following evaluation of the TOR memo:

- Several of the scenarios presented in the TOR memo are supportive to the TOR estimates presented in the RD/RAWP. Several scenarios provide TOR estimates in a similar range to the scenario modeled in Appendix E of the RD/RAWP.
- As part of sensitivity analysis, some TOR estimates are presented that significantly exceed the estimates presented in the RD/RAWP. However, these estimates should be viewed in the context of sensitivity analysis to determine the significance of different input parameters on estimates. Scenarios that combined several conservative inputs and approaches obviously result in increased TORs. However, the basis presented in the TOR memo to conclude that these scenarios are more likely to be representative than other scenarios is limited, and it is likely these scenarios represent extreme cases that are not representative of actual conditions.
- The combining of conservative inputs in a TOR scenario results in a compounding effect that results in long TOR estimates. A graphical distribution of TOR estimates with varying inputs above and below estimated values would be expected to be constrained close to zero and show a long tail extending to hundreds of years (i.e., it would not be bell curve but have an early peak and a long tail). Therefore, even though there are scenarios presented that extend out hundreds of years based on compounding conservative inputs, scenarios with reasonable inputs should not be expected to result in TORs that fall significantly higher than the TOR estimated in the RD/RAWP.
- The LE LNAPL dissolution model/boundary conditions are likely appropriate under the proposed EBR flow conditions. Both the flow rates under EBR and the enhancement of dissolution under active bioremediation indicate the use of the NE condition using data from the non-reactive MTT is inappropriate for the screening of EBR as supported by several studies (Amos, 2008; Bahar et al, 2016; Cope, 2001; Chu et al, 2006; and Seagren et al, 1999).
- The TOR memo supports the need to implement Phase 1 of EBR and collect data under actual EBR conditions for further analysis.

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